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Mechanism for diamond nucleation and growth on single
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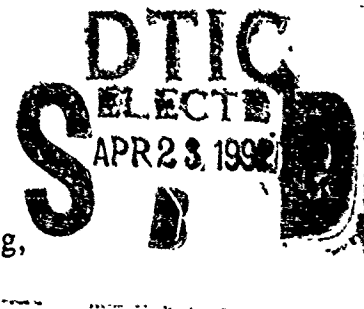
by

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13. ABSTRACT (Maximum 200 words) The nucleation and growth of diamond crystals on single crystal copper surfaces implanted with carbon ions has been studied. Microwave plasma enhanced chemical vapor deposition was used for diamond growth. The single crystal copper substrates were implanted either at room temperature or at elevated temperature (~820 °C) with carbon ions prior to diamond nucleation. This procedure leads to the formation of a graphite film on the copper surface which greatly enhances diamond crystallite nucleation. From our study we construct a simple lattice model for diamond growth on graphite as <111> _{diamond} parallel to <0001> _{graphite} and <110> _{diamond} parallel to <1120> _{graphite} .				
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Mechanism for diamond nucleation and growth on single crystal copper surfaces implanted with carbon

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The nucleation and growth of diamond crystals on single-crystal copper surfaces implanted with carbon ions has been studied. Microwave plasma-enhanced chemical vapor deposition was used for diamond growth. The single-crystal copper substrates were implanted either at room temperature or at elevated temperature ($\sim 820^\circ\text{C}$) with carbon ions prior to diamond nucleation. This procedure leads to the formation of a graphite film on the copper surface which greatly enhances diamond crystallite nucleation. From our study we construct a simple lattice model for diamond growth on graphite as $\langle 111 \rangle_{\text{diamond}}$ parallel to $\langle 0001 \rangle_{\text{graphite}}$ and $\langle 110 \rangle_{\text{diamond}}$ parallel to $\langle 11\bar{2}0 \rangle_{\text{graphite}}$.

The unique properties of diamond make it one of the most desirable materials for high power electronic devices.¹ However, the technology of high-quality single-crystal diamond film growth thus far is only limited to homoepitaxy.² Diamond nucleation on nondiamond substrates is very difficult due to the extremely high surface energy of diamond.^{3,4} An attempt to grow epitaxial diamond film on single-crystal nickel substrates has been carried out⁵ without success. Koizumi *et al.*⁶ reported that diamond can be grown heteroepitaxially on single-crystal *c*-BN substrate; however, a large single crystal of *c*-BN is even harder to come by than diamond itself. Copper is considered to be the next best candidate for the substrate. Unlike Ni, Mo, W, Fe, or Si, Cu does not form carbide when it interacts with carbon.

In this letter, we present our study of the nucleation and growth of diamond on modified surfaces of single crystal Cu (100) and (111). Carbon ion implantation was carried out on the Cu substrates prior to diamond growth in order to increase the surface energy. The Cu crystals were implanted by carbon ions to doses of 1×10^{18} ions/cm² at temperatures in the range of 25 to 840 $^\circ\text{C}$ and at energies of 70 and 120 keV. Implantation at elevated temperature ($\sim 800^\circ\text{C}$) leads to the diffusion of implanted carbon to the surface where a graphite film is formed during implantation.⁷ During room-temperature implantation, the carbon is embedded ~ 1500 Å deep for an ion energy of 125 keV. During subsequent thermal annealing at elevated temperature ($\sim 800^\circ\text{C}$) the embedded carbon will diffuse to the surface and form a graphite layer.

The Cu crystals were grown using the Bridgman technique. Diamond growth was carried out by microwave plasma-enhanced chemical vapor deposition (MPECVD) using a tubular 2.45 GHz microwave plasma reactor. The typical deposition conditions used were: 3% CF₄ or 0.5% CH₄ and 0.7% O₂ in 200 sccm H₂, 33 Torr, 800 $^\circ\text{C}$, 340 W microwave power.

The implantation of carbon ions (70 keV, 1×10^{18} ions/cm², 820 $^\circ\text{C}$) leads to the formation of a rough carbon film consisting of 20–30 μm size islands (~ 900 Å thick) on the Cu surface, as shown by the optical micrograph in Fig. 1. Rutherford backscattering (RBS) and channeling analysis shows that the carbon is mostly on the substrate surface. X-ray diffraction analysis reveals that the carbon layer is graphitic, with the *c* axis of the hexagonal graphite lattice perpendicular to the Cu surface within one degree.

Transmission electron microscopy (TEM) analysis further confirms the structure of the carbon films formed by ion implantation at elevated temperature. Figure 2 shows the TEM micrograph and its corresponding diffraction pattern. The streaks which form rings around the six-spot pattern suggest that the graphite consists of turbostratic layers⁷ formed by the carbon dissolution-precipitation mechanism.^{8,9} This finding is in agreement with the results reported in Ref. 7, but is contrary to the report in Ref. 10 which claimed that an epitaxial diamond layer was formed by the ion implantation technique.

Note in Fig. 2(a) that the film develops some cracks which originate from the difference in the coefficient of thermal expansion between graphite and Cu.¹¹ The cracks result in the two diffraction spots near the incident beam. They are indexed [see Fig. 2(b)] as the (0002) reflections of graphite indicating that the prism planes of graphite at the cracks are almost parallel to the Cu surface.

Diamond nucleation had been attempted on both pure and carbon implanted Cu. The diamond crystals obtained on either surface are polycrystalline. No indication of epitaxial growth or growth with preferred orientation has been observed. The graphite layer on the Cu surface is found to enhance diamond nucleation quite significantly. This is shown by the optical micrographs in Fig. 3 which depicts the preferential nucleation of diamond crystals on the graphite "dots" formed on the Cu crystal surface by carbon implantation through a Ta shadow mask at 840 $^\circ\text{C}$. Following implantation, the diamond crystals were deposited using 3% CF₄ and 0.7% O₂ in H₂. Figure 3 also shows that the diamond crystals are preferentially found near the

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10p

20p

FIG. 1 Optical micrograph of a carbon layer formed by carbon ion implantation into Cu(100) surface at 820 °C, 1×10^{16} ions/cm² dose, and 70 keV.

edges of the graphite islands implying some interesting chemistry involved in the diamond deposition reactions on graphitic surfaces. We also observe massive nucleation of diamond crystals on the edges of the graphite cracks.

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FIG 2 (a) Plan view transmission electron micrographs (bright field) of a carbon layer formed by carbon ion implantation into Cu(111), taken using Hitachi H-700 at 200 kV (b) the corresponding diffraction pattern

FIG 3. Preferential nucleation of diamond crystals on the edges of graphite islands on Cu(111): (a) low magnification, (b) high magnification. The circle patch of the graphitic islands were formed by C implantation through a Ta shadow mask at the following conditions: 75 keV, 1×10^{16} ions/cm² dose, and 840 °C.

Diamond crystals can be grown on Cu implanted by carbon at room temperature, but the crystals are smaller than those grown on substrates implanted at elevated temperature (for similar deposition conditions). The size difference is believed to be related to the time required for the implanted carbon to diffuse to the surface where it forms a graphite layer which enhances nucleation of diamond crystals during deposition. Diamond crystals obtained by this method were found to be polycrystalline also.

To confirm that diamond nucleates and grows on the graphite edges of the planes, we studied the growth of diamond on highly oriented pyrolytic graphite (HOPG) crystals. Similarly, diamond crystals were found to nucleate primarily at the edges of the graphite sheet. A striking difference in the diamond nucleation density on the basal and prism planes of graphite was clearly observed, as shown in Fig. 4. This can be understood from the fact that the bonding on the basal plane of graphite lattice is saturated with the very strong π (sp^2) C—C bonding. Each carbon at the prism plane, however, has one dangling bond result in a lower bond strength. Previous studies of the reaction of graphite with atomic hydrogen¹² have shown strong evidence that the carbon-carbon bonding on the edges of the carbon sheets represent the weakest and thus the most reactive sites in the whole graphite lattice. This is

10 op

FIG 4 Scanning electron micrographs showing the distinct difference in diamond nucleation density on (a) the prism and (b) basal planes of HOPG crystals

21p

FIG. 5. A simple model of diamond nucleus on the edge of graphite basal plane: $\langle 111 \rangle_{\text{diamond}} // \langle 0001 \rangle_{\text{graphite}}$ $\langle 110 \rangle_{\text{diamond}} // \langle 1120 \rangle_{\text{graphite}}$

confirmed by our study of graphite etching with atomic hydrogen.¹³

It is therefore reasonable to assume that diamond nucleation on graphite is first initiated by hydrogenating the carbon atoms at the graphite edge to form sp^3 hybridized CH_3 bonds. This is done through the disruption of carbon atoms in the $\{112L\}$ planes.¹⁴ This is then followed by reaction with hydrocarbon radical precursors from the gas phase to form diamond. From these results of our study we construct a simple lattice model of a diamond nucleus on the edge of the graphite lattice. This is shown in Fig. 5. According to the proposed model, the $\{111\}$ plane of diamond is perpendicular to the basal plane of graphite and the $\langle 110 \rangle_{\text{diamond}}$ is parallel to the $\langle 1120 \rangle_{\text{graphite}}$. This model is based on the fact that the carbon-carbon length in the $\langle 110 \rangle$ direction of diamond (2.507 Å) matches that in the $\langle 1120 \rangle$ direction of graphite (2.459 Å) within 2%. In the high-pressure synthesis of diamond from graphite, the row of carbon atoms along the $\langle 1120 \rangle$ of graphite is believed to

transform into the $\langle 110 \rangle$ of diamond.¹⁵ The model also agrees with the previous study of graphite formation on CVD diamond films¹⁶ in which graphite was found to form with its basal plane matches on or close to the $\{111\}$ planes of diamond.

In conclusion, diamond crystals have been grown on carbon-implanted single-crystal copper surfaces. The structure of the diamond is polycrystalline. The diamond crystals are found to nucleate preferentially on the prism planes of the graphite layer on top of the Cu surface. A simple model of diamond crystal growth on graphite surfaces is proposed based on the lattice matching between $C-C_{\text{graphite}(1120)}$ and $C-C_{\text{diamond}(110)}$ and graphite edge chemistry. A detailed study of carbon precipitation onto Cu surfaces is very important to determine whether diamond can be grown epitaxially on the substrate.

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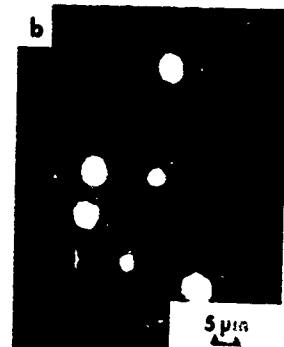
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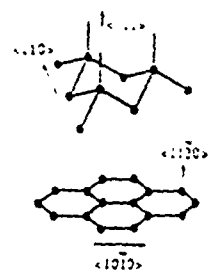


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